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Theoretical studies of clean and hydrogenated diamond (100) by molecular mechanics

by

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# Theoretical studies of clean and hydrogenated diamond (100) by molecular mechanics

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## Abstract

The atomic structure and energetics of the clean (100)-(2×1), (100)-(2×1):H monohydride, (100)-(1×1):2H full dihydride, (100)-(3×1):1.33H intermediate dihydride, and other intermediate hydride surfaces obtained by local removal of H atoms from or addition of H atoms to the (2×1) monohydride, are investigated by molecular mechanics (MM3). The monohydride phase is found to be the most stable thermodynamically and is predicted to be the dominant phase under chemical vapor deposition conditions. Gas-surface reactions relevant to diamond chemical vapor deposition involving hydrogen and the diamond (100)-(2×1):H surface are discussed in light of the derived energetics.

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## I. INTRODUCTION

In the past few years, our understanding of the low-pressure growth of diamond by chemical vapor deposition (CVD) has been greatly enhanced due to intensive research efforts.<sup>1</sup> Much has been learned about the gas phase chemistry during diamond CVD<sup>2</sup> and the identity of the primary growth precursor(s),<sup>3</sup> particularly for hot-filament CVD. Correspondingly, many mechanistic models based on the observed gas-phase species, such as methyl radical<sup>4</sup> and acetylene,<sup>5</sup> have been proposed to account for diamond growth at the molecular level. In contrast, very little is known about the chemistry on the diamond surfaces, especially under growth conditions. In most of the mechanistic models thus far proposed, very simple assumptions about the atomic structure of the surfaces under growth conditions are made and the kinetics and thermodynamics of surface reactions are estimated from gas-phase reactions. It is clear that considerably more experimental and theoretical work will be required to understand diamond growth at the molecular level.

Among the three low-index surfaces of diamond, i.e., (111), (110), and (100), the diamond (100) orientation is unique because nearly-atomically-smooth surfaces, critical to comparison between experiment and theory, have been obtained only on the (100) face by homoepitaxial CVD growth.<sup>3d,6-8</sup> Moreover, each of carbon atoms on the ideal (100) surface has two dangling bonds (unpaired electrons) while on ideal (110) and (111) surfaces each surface carbon atom has only one dangling bond, thus rendering rich and yet, up to now, very confusing chemistry which provides a challenge for both experiment and theory. Experimental studies of diamond (100) have been carried out by low-energy electron diffraction (LEED),<sup>9-11</sup> temperature-programmed desorption (TPD),<sup>10,11</sup> photon-stimulated ion desorption (PSID),<sup>12</sup> electron-stimulated desorption time of flight (ESD-TOF) spectroscopy,<sup>10</sup> photoemission,<sup>10</sup> and Rutherford backscattering spectroscopy (RBS).<sup>13</sup> But many important questions, such as the surface hydrogen coverage, assignment of TPD desorption peaks, and stability of hydride phases, are still issues of debate. On the theoretical side, various authors have utilized semiempirical<sup>14-17</sup> and empirical approaches<sup>18,19</sup> to investigate the properties of clean and hydrogenated diamond (100). But substantial discrepancies remain, in both the dimer bond length ( $\pm 0.1$  Å) and in the energetics, and a satisfactory description of the chemisorption and reaction of hydrogen on diamond (100) is not yet possible.

We recently demonstrated the usefulness of the empirical molecular mechanics (MM3) method, developed by Allinger and co-workers over the past two decades,<sup>20,21</sup> in studying the surface chemistry of diamond (100).<sup>22</sup> A closely-related approach has been taken by Harris and Belton in calculations on diamond (111) and (110) surfaces.<sup>23</sup> Molecular mechanics is arguably the most successful and certainly the most widely used of the empirical potentials available, and several versions are commercially available. In the present paper, further thermochemical analysis is performed on the previous results, and several additional hydride structures are considered. Recent

near-atomic-resolution images of CVD-grown diamond (100), obtained by scanning tunneling microscopy<sup>7</sup> and atomic force microscopy,<sup>8</sup> show evidence of a (2×1) reconstruction, presumably associated with the so-called monohydride structure with one hydrogen atom per surface carbon atom and a dimer bond between pairs of surface carbon atoms.<sup>7-10,14-19,22</sup> Because of the likely importance of the monohydride surface in CVD growth, H atom abstraction and insertion reactions on this particular surface are studied by molecular mechanics as well. Several gas-surface reactions important in CVD growth are discussed in light of the derived energetics.

## II. THEORETICAL METHOD AND RESULTS

The calculation method used to calculate the structures and enthalpies of formation of the diamond (100)-(2×1), (100)-(2×1):H, (100)-(3×1):1.33H, and (100)-(1×1):2H surfaces has been described in detail previously.<sup>22</sup> The third-generation MM3 force field, with parameters for saturated, unsaturated, and conjugated hydrocarbons, has a demonstrated high degree of accuracy (bond lengths  $\approx \pm 0.01$  Å, bond angles between atoms other than hydrogen  $\approx \pm 1^\circ$ , torsional angles  $\approx \pm 4^\circ$ , heats of formation  $\approx \pm 1$  kcal/mol) for small, large, and highly strained molecules and bulk diamond as well.<sup>20,21</sup> MM3 should be applicable to the description of saturated, unsaturated, and conjugated hydrocarbon species on any crystal face of diamond as long as the bond lengths, bond angles, and distances between nonbonded atoms are within the range of values in structures for which MM3 has demonstrated accuracy. MM3 parameters for radicals are tentative,<sup>21</sup> making calculations with open-shell species more uncertain, and MM3 cannot describe surface species with bonding configurations that have not been parameterized in molecules.

Briefly, atomic positions are determined by minimizing an empirical potential energy function, the so-called steric energy  $E$ ,<sup>20,21</sup> subject to periodic boundary conditions<sup>22</sup> and a substrate lattice constant fixed at the value of bulk diamond.  $E$  is given by

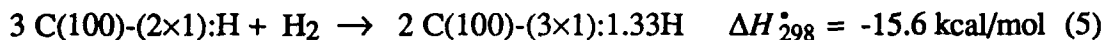
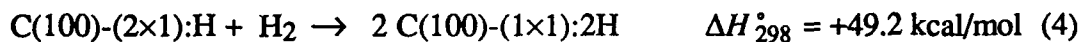
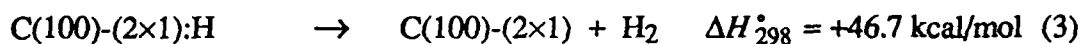
$$E = \sum E_s + \sum E_\theta + \sum E_\omega + \sum E_{s\theta} + \sum E_{\omega s} + \sum E_{\theta\theta'} + \sum E_{vdW} + \sum E_{dpl} \quad (1)$$

where  $E_s$  is the bond stretching energy,  $E_\theta$  is the angle bending energy,  $E_\omega$  is the torsional energy;  $E_{s\theta}$  is the stretch-bend energy,  $E_{\omega s}$  is the torsion-stretch energy,  $E_{\theta\theta'}$  is the bend-bend coupling energy;  $E_{vdW}$  is the van der Waals repulsion energy between nonbonded atoms, and  $E_{dpl}$  is the dipole-dipole interaction energy.<sup>20,21</sup> The enthalpy of formation is calculated by adding bond enthalpies ( $\Delta H_{\text{bond}}$ ) and functional-group correction terms ( $\Delta H_{\text{struct}}$ ) to the minimized steric energy:

$$\Delta H_f^\circ = \Delta H_{\text{bond}} + \Delta H_{\text{struct}} + E. \quad (2)$$

For completeness and comparison to the new results, scale drawings of the structures of the clean (100)-(2×1), (100)-(2×1):H monohydride, (100)-(1×1):2H full dihydride, and (100)-

(3×1):1.33H partial dihydride surfaces are presented in Figure 1, with selected bond lengths (Å) and angles given explicitly. The calculated energetics of these structures are described by the following enthalpies of reaction at 298 K, expressed with respect to the (2×1):H monohydride:<sup>22</sup>



We have also calculated temperature-dependent enthalpies, entropies, and free energies of reaction for Eqs. (3-5), enabling estimation of equilibrium concentrations under CVD conditions:

$$\Delta H^\circ(T) = \Delta H_{298}^\circ + \int_{298}^T \Delta C_p^\circ dT' \quad (6)$$

$$\Delta S^\circ(T) = \Delta S_{298}^\circ + \int_{298}^T \Delta C_p^\circ d \ln T' \quad (7)$$

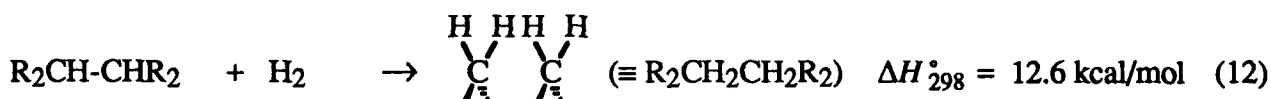
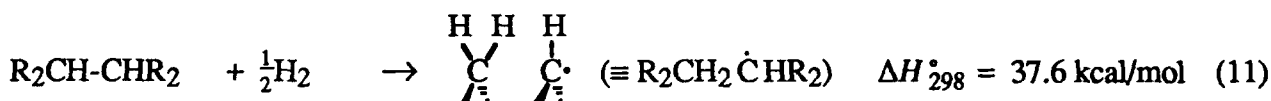
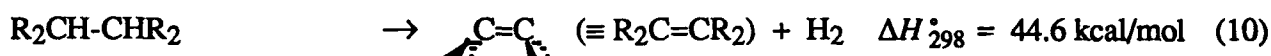
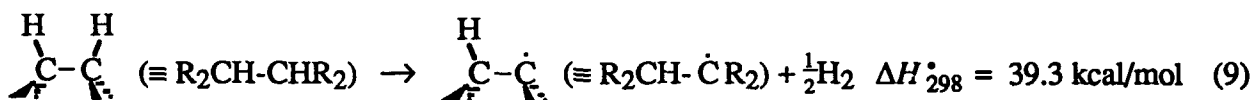
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

Typically, entropy and heat capacity changes are only weakly dependent on the steric energy, and we have estimated  $\Delta S_{298}^\circ$  and  $\Delta C_p^\circ$  for gas-surface reactions (3-5) at various temperatures using the group additivity method.<sup>24</sup> The results are summarized in Table I.  $\Delta H^\circ$  is only weakly temperature-dependent, and therefore small errors in  $\Delta C_p^\circ$  are inconsequential. The largest contribution to  $\Delta S_{298}^\circ$  in Eqs. (3-5) comes from the lost translational entropy of gas-phase  $\text{H}_2$ , and therefore the group additivity estimates should be fairly accurate. In cases where the steric energy is *not* small, e.g., the (1×1):2H dihydride, the group additivity estimates are much less accurate. The entropy associated with opening polycyclic ring systems is difficult to estimate using group additivity, as pointed out by Harris *et al.*,<sup>23a</sup> and the  $\Delta S$  estimates for reactions (4) and (5) may be uncertain by 5-10 cal mol<sup>-1</sup> K<sup>-1</sup>.

We believe, based on the currently available experimental evidence<sup>7,8,11</sup> and the present theoretical work, that the (2×1):H monohydride surface (Fig. 1(b)) is the predominant species under typical hot-filament or microwave plasma CVD growth conditions. Therefore, we have performed MM3 calculations on surfaces which are related to the monohydride by removal or addition of hydrogen atoms due to abstraction by or insertion of gas-phase H atoms, respectively. In contrast to our previous study,<sup>22</sup> we have chosen the (100)-(2×1):H monohydride surface as the reference state, so that the surface steric energy is defined as the difference between the steric energy of species obtained by removal or addition of H atoms on the monohydride and the steric energy of the monohydride itself.

The slab chosen for the initial and modified diamond (100)-(2×1):H monohydride surfaces was 5 layers thick, consisting of 3×4 (2×1) unit cells with a total of 123 carbon atoms.<sup>22</sup> To simplify the minimization of the surface steric energy, we allowed only the surface atoms (C and H) in the unit cell which either loses or gains H atoms to relax and fixed the remainder of the atoms in their monohydride surface positions. The surface energy calculated in this way is estimated to be approximately 2-3 kcal/mol less accurate than that obtained by complete relaxation of the surface atoms. An additional uncertainty of about ±3 kcal/mol for radical surface species is estimated.

The surface species formed by simple removals or additions of hydrogen atoms on the (100)-(2×1):H monohydride surface are summarized in Eqs. (9-12) below, together with a shorthand notation ("R" denotes a backbond to second-layer lattice atoms) and the calculated enthalpies of formation from the monohydride.



In reaction (9), a single hydrogen atom is removed from a monohydride surface dimer, creating a radical site, while both hydrogen atoms are removed in reaction (10), forming a strained dimer  $\pi$  bond. In reaction (11) the dimer bond is broken and a hydrogen atom is added to one of the carbon atoms, while reaction (12) represents a hydrogenolysis of the dimer C-C bond. In each of these structures, all surrounding dimers remain in the (2×1):H monohydride configuration. The calculated atomic structures of  $\text{R}_2\text{CH}-\dot{\text{C}}\text{R}_2$ ,  $\text{R}_2\text{C}=\text{CR}_2$ ,  $\text{R}_2\text{CH}_2-\dot{\text{C}}\text{HR}_2$ , and  $\text{R}_2\text{CH}_2\text{CH}_2\text{R}_2$  are given in Fig. 2(a-d), respectively, and the displacements of atoms from their ideal bulk-terminated positions are presented in Table II.

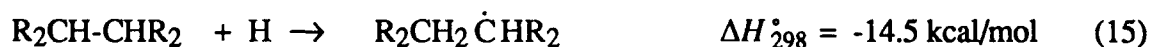
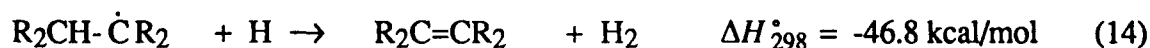
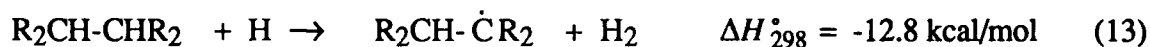
### III. DISCUSSION

A detailed discussion of the structure and energetics of the clean (100)-(2×1), (100)-(2×1):H monohydride, (100)-(1×1):2H full dihydride, and (100)-(3×1):1.33H partial dihydride surfaces (Fig. 1) has been presented elsewhere.<sup>22</sup> Briefly, the structures are in reasonable agreement overall (± 0.1 Å in bond lengths) with the recent semiempirical results of Verwoerd<sup>14</sup> and of Mehandru and

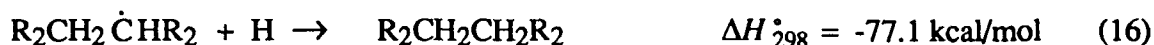
Anderson<sup>16</sup> and the empirical results of Brenner,<sup>19</sup> with larger discrepancies in the energetics. The demonstrated performance of MM3 for a wide range of hydrocarbons<sup>20</sup> suggests that our results are the most accurate of the existing surface calculations for structures with bond lengths and bond angles in the range known to be well described by MM3 (a similar limitation applies to semiempirical theories and other empirical potentials). The (1×1):2H full dihydride and, to a lesser extent, the clean (100)-(2×1) structures have parameters (nonbonded H-H distance and C=C bond length, respectively) that lie outside the established range, and our calculations are less reliable than for the (2×1):H and (3×1):1.33H structures. The very recent semiempirical calculations of Zheng and Smith<sup>17</sup> show substantial discrepancies from the aforementioned studies,<sup>14,16,19,22</sup> including significantly shorter C-C dimer bond lengths and a prediction of a highly stable (100)-(1×1):2H dihydride ( $\Delta H^\circ$  at 0 K = -86.6 kcal/mol for reaction (4)<sup>17</sup>).

It is apparent from Table I that among the three possible diamond surface hydride phases, the monohydride phase is the most stable over the temperature range of 298-1500 K, followed in stability by the clean surface, which suggests that the monohydride is the dominant surface species at the typical growth temperatures of 1073-1273 K.<sup>1</sup> Recent STM,<sup>7</sup> AFM,<sup>8</sup> and LEED<sup>11</sup> investigations on homoepitaxial diamond (100) films transferred and/or analyzed in air have clearly observed a (2×1) reconstruction with dimer rows and steps, which each set of authors has attributed to the monohydride.<sup>7,8,11</sup> While observation of a surface structure after growth and air exposure does not prove that the structure was present under growth conditions, it is strongly suggestive, particularly when that structure is a stable one and its appearance is insensitive to the details of growth and reactor shutdown conditions, as evidenced by its observation by several research groups. Since less-stable structures like the (3×1):1.33H and (1×1):2H dihydrides are favored at lower temperatures, if they did exist under growth conditions they would likely be stable as growth was quenched and the substrate was cooled. The fact that they are not observed provides indirect evidence that they also do not exist in large concentrations under growth conditions and that the (2×1):H monohydride predominates, with clean (2×1) dimers perhaps also being important.

An important role for dihydride phases on diamond (100) has been suggested by several authors.<sup>4b,10,17</sup> Dihydride species are presumably generated in a local, stepwise manner from the monohydride by reaction with atomic hydrogen, so it is appropriate to first consider the local modifications of the (2×1):H monohydride illustrated in Fig. 2. The energetics of these interconversions follow directly from Eqs. (9-12) and the heat of formation of H (52.10 kcal/mol<sup>25</sup>):







When a H atom on the (2×1) monohydride surface is abstracted by a gas-phase H atom, as in reaction (13), a radical site is formed on the surface. The radical C atom moves towards the dimer center and slightly upward from the (2×1):H position towards a more favorable  $\text{sp}^2$  geometry, while the neighboring C on the same dimer moves away from the dimer center. The change in enthalpy associated with abstraction of H from the monohydride surface, -12.8 kcal/mol, is similar to but somewhat more negative than the value associated with abstraction of the tertiary hydrogen atom from isobutane to form a *tert*-butyl radical, -8.4 kcal/mol.<sup>26</sup> The difference is likely due to release of some of the strain in the monohydride. Brenner,<sup>19</sup> using an empirical Tersoff-type potential, obtained -10.0 kcal/mol for the same abstraction reaction. Since his potential was constructed using atomization energies of hydrocarbon molecules at 0 K, a temperature correction should be made to his value in order to make a direct comparison with our value. Brenner also found that the enthalpy of abstraction of one H atom from the diamond (111)-(1×1):H monohydride surface was nearly the same ( $\Delta H = -11$  kcal/mol) as on the (100) face. In both cases, the H atom is attached to a tertiary carbon atom and therefore the abstraction enthalpies should be similar. Both the present results and those of Brenner<sup>19</sup> support the applicability of gas phase kinetic and thermodynamic data to simulation of diamond growth kinetics<sup>4b,4d,23,27</sup> but also indicate that the energetics can easily differ by several kcal/mol between analogous molecular and surface species.

Both the structure and energetics of the  $\text{R}_2\text{C}=\text{CR}_2$  species formed by removal of *two* hydrogen atoms from the (2×1):H monohydride are quite similar to those of the clean surface, indicating that our present assumption of no subsurface relaxation is not too severe. For comparison, we calculate a dimer bond length of 1.48 Å in  $\text{R}_2\text{C}=\text{CR}_2$  (surrounded by  $\text{R}_2\text{CH}-\text{CHR}_2$  in adjacent unit cells) versus 1.46 Å on the clean surface (all  $\text{R}_2\text{C}=\text{CR}_2$ ). The heats of reaction for  $\text{R}_2\text{CH}-\text{CHR}_2 \rightarrow \text{R}_2\text{C}=\text{CR}_2 + \text{H}_2$  for the isolated  $\text{R}_2\text{C}=\text{CR}_2$  and clean surface cases were also very similar at 44.6 and 46.7 kcal/mol, respectively. The slightly lower enthalpy of the isolated  $\text{R}_2\text{C}=\text{CR}_2$  may be due to weak interactions between the double bond and hydrogen atoms in adjacent unit cells.

Considerably less energy is required to remove the second hydrogen atom on the dimer than the first, as evidenced by a much more negative abstraction reaction enthalpy, -46.8 kcal/mol (Eq. (14)). Put differently, we calculate the first C-H ( $\text{R}_2\text{CH}-\text{CR}_2\text{-H}$ ) bond enthalpy to be 91.4 kcal/mol (similar to *t*-C<sub>4</sub>H<sub>9</sub>-H, 95.8 kcal/mol<sup>25</sup>), while the second C-H ( $\text{R}_2\dot{\text{C}}-\text{CR}_2\text{-H}$ ) bond enthalpy is only 57.4 kcal/mol. For comparison, the C-H bond enthalpies in the molecular radicals  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{-H}$ ,  $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{-H}$ , and  $(\text{CH}_3)_2\dot{\text{C}}\text{CH}_2\text{-H}$  are all between 36.0 and 36.5 kcal/mol. The higher C-H bond energy associated with the surface species is mainly due to the strain present in the abstraction product ( $\text{R}_2\text{C}=\text{CR}_2$ , Fig. 2b)--the surface dimer is unable to form as strong a double bond as in free molecules. Brenner calculated a similar  $\Delta H$  for reaction (14), -50 kcal/mol at 0 K.<sup>19</sup>

The implication of the much weaker C-H bond in  $R_2CH-\dot{C}R_2$  is that H-atom vacancies will tend to occur in pairs, so that under growth conditions the (100) surface is likely to consist predominantly of (2×1):H monohydride dimers and  $R_2C=CR_2$  dimers rather than isolated radical sites. One mechanism for loss of the second H, which to our awareness has not yet been considered in (100) growth models, is atomic desorption, analogous to  $\beta$ -scission in molecules:



Assuming no activation barrier for the reverse reaction, so that the activation energy is equal to the enthalpy of reaction, and a preexponential factor of  $10^{13} \text{ s}^{-1}$ , we estimate a rate constant of  $200 \text{ s}^{-1}$  for reaction (17) at a substrate temperature of  $900^\circ\text{C}$ , which is likely to be important. Another likely process is H migration to an adjacent radical site, resulting in:



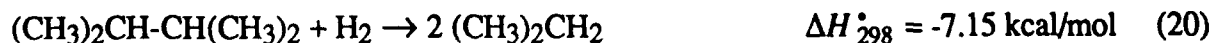
The driving force for pairing of hydrogen atoms (and vacancies) on dimers is a direct consequence of the  $\pi$ -bond in unoccupied dimers. We have recently noted a similar tendency for double-occupation of surface dimers on Si(100), although there the energetic driving force is much less.<sup>28</sup>

Turning to the products of H atom addition to the monohydride, we see that steric repulsion of hydrogen perturbs the structure and energetics but is much less dominant than on the full (1×1):2H dihydride. The H1'-C2-H2' bond angle ( $101.5^\circ$ ) in  $R_2CH_2\dot{C}HR_2$  (Fig. 2(c)) is only slightly less than the unstrained value of  $106.7^\circ$ ,<sup>20a</sup> and the orientation of the C1-H1 bond is only slightly perturbed from that of an unstrained secondary radical.<sup>29</sup> The enthalpy change for reaction (15) is slightly more favorable than that for the analogous reaction of 2,3-dimethylbutane:



This implies that the reduction in strain energy achieved by breaking the dimer bond is slightly larger than the increase in H-H repulsion energy.

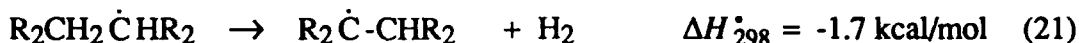
Steric H-H repulsion is more important in the  $R_2CH_2CH_2R_2$  structure (Fig. 2(d)), causing considerable distortions in the C-H bond angles. Also indicative of steric repulsion in the  $R_2CH_2CH_2R_2$  surface species is the observation that  $\Delta H$  for reaction (12) is some 20 kcal/mol more positive than that for



despite the release of strain energy in the monohydride. On the other hand, reaction (12) is much less unfavorable than reaction (4), forming the (1×1):2H full dihydride, in which the H-H steric repulsion is extreme. Two isolated dihydride units can reduce their steric repulsion by simply tilting away from one another, which is prevented in the (1×1):2H structure by adjacent dihydride units.

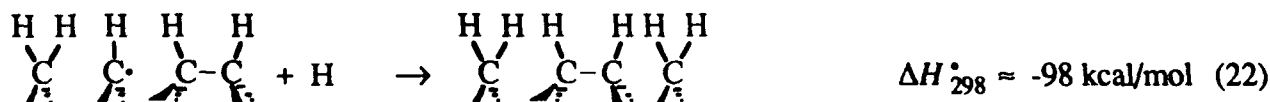
Although reactions (15) and (16), which result in hydrogenolysis of the dimer bond to form two neighboring dihydride species, have favorable energetics, we suggest that they may be minor processes under CVD conditions and that dihydrides will only exist in very low concentrations on flat (100) terraces (but still could exist at steps and defect sites). Focusing first on reaction (15), insertion of a H atom into the dimer bond, a rough estimate of the entropy of reaction follows from the lost translational entropy of the gas-phase H atom,  $\approx -27.7 \text{ cal/mol K}^{-1}$ ,<sup>24</sup> implying  $\Delta G^\circ \approx -6 \text{ kcal/mol}$  at 298 K. At the elevated temperatures typical of CVD growth,  $\Delta G^\circ$  will become positive (cf. Table I), implying a small equilibrium constant for reaction (15). An additional difficulty with reaction (15) is that analogous reactions in the gas phase are simply not known--abstraction reactions (cf. Eq. (13)) dominate. The transition state associated with reaction (15) would be interesting, most likely involving a 5-coordinated carbon atom or bridge-bonded H, but has not been established.

Assuming that  $\text{R}_2\text{CH}_2\dot{\text{C}}\text{HR}_2$  can be produced by reaction (15), the dihydride could be stabilized by a radical recombination reaction (e.g., Eq. (16)). Several kinetic processes would compete with the recombination, however. An H atom could migrate to an adjoining  $\text{R}_2\text{CH}-\dot{\text{C}}\text{R}_2$  site. Alternatively,  $\text{H}_2$  loss by  $\alpha$ -elimination may be possible:



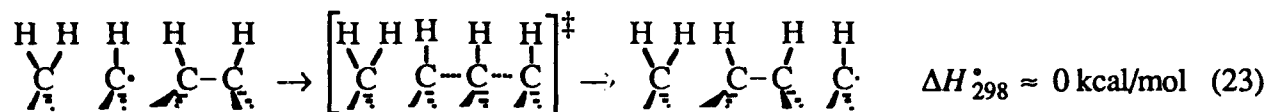
The heat of reaction for reaction (21) follows by subtracting reaction (9) from reaction (11). Again, an analogous gas phase reaction is not known, and the rate constant cannot be easily estimated. Taking the entropy of  $\text{H}_2$  in the standard state,  $29.5 \text{ cal/mol K}^{-1}$ ,<sup>24</sup> as a rough estimate of the reaction entropy, we obtain  $\Delta G^\circ_{298} \approx -10.5 \text{ kcal/mol}$  for reaction (21), indicating a small *equilibrium* concentration of  $\text{R}_2\text{CH}_2\dot{\text{C}}\text{HR}_2$ .

More-stable dihydride ( $\text{CH}_2$ ) units separated by monohydride dimer units could be generated via several pathways. Formation of  $\text{R}_2\text{CH}_2\text{CH}_2\text{R}_2$  followed by a double migration of a hydrogen atom to an adjacent  $\text{R}_2\text{CH}-\text{CHR}_2$  dimer seems unlikely, as the first migration step,  $\text{R}_2\text{CH}_2\text{CH}_2\text{R}_2 + \text{R}_2\text{CH}-\text{CHR}_2 \rightarrow 2 \text{R}_2\text{CH}_2\dot{\text{C}}\text{HR}_2$ , is quite unfavorable ( $\Delta H^\circ_{298} = 62.6 \text{ kcal/mol}$ ). A more likely pathway involves reaction (13) occurring on adjacent dimers:



The estimate of the heat of reaction for reaction (22) follows from the heats of formation of  $\text{R}_2\text{CH}_2\dot{\text{C}}\text{HR}_2$  (Eq. (9)) and the (3 $\times$ 1):1.33H dihydride (Eq. (5)) from the monohydride, and is virtually identical to the negative of a secondary C-H bond enthalpy.<sup>26</sup> Formation of dihydride

units separated by more than one monohydride dimer could result from "migration" of the radical center by rearrangement of C-C dimer bonds:



The concentration of (3×1)-type dihydride units will be determined by the concentration of  $\text{R}_2\text{CH}_2\dot{\text{C}}\text{HR}_2$  and by competition between reaction (22) and abstraction of H in the dihydride by incident H atoms, but our estimates of  $\Delta G^{\circ}$  (Table I(c)) suggest that under growth conditions their concentration will be low.

We suggest that dihydride formation may result from reactions (15), (22), and (23), but the kinetics of these reactions are highly uncertain at present. It is noteworthy that Thomas *et al.*<sup>11</sup> had difficulty finding evidence for formation of the dihydride. Further experiments are clearly required, and quantum chemical estimates of the activation barriers to reactions (15), (22), and (23) would be very illuminating. Finally, accurate first-principles quantum mechanical calculations of the structure and energetics of selected surface species are needed to establish the degree of accuracy of MM3 as applied to surface chemistry on diamond.

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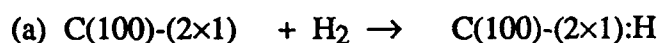
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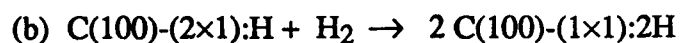
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## TABLES

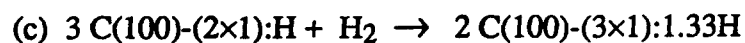
TABLE I. Thermochemical properties of diamond(100)-hydrogen reactions.



$T$ (K)	$\Delta H^\circ$ (kcal/mol)	$\Delta S^\circ$ (cal/mol K <sup>-1</sup> )	$\Delta G^\circ$ (kcal/mol)
298	- 46.7	- 28.5	- 38.2
400	- 47.2	- 29.9	- 35.2
500	- 47.4	- 30.4	- 32.2
600	- 47.6	- 30.4	- 28.3
800	- 47.5	- 30.6	- 23.1
1000	- 47.1	- 28.6	- 18.5
1500	- 46.3	- 27.9	- 4.4



$T$ (K)	$\Delta H^\circ$ (kcal/mol)	$\Delta S^\circ$ (cal/mol K <sup>-1</sup> )	$\Delta G^\circ$ (kcal/mol)
298	49.2	- 11.6	52.7
400	49.9	- 9.6	53.7
500	50.4	- 8.5	54.7
600	50.7	- 7.9	55.4
800	51.2	- 7.2	57.0



$T$ (K)	$\Delta H^\circ$ (kcal/mol)	$\Delta S^\circ$ (cal/mol K <sup>-1</sup> )	$\Delta G^\circ$ (kcal/mol)
298	- 15.6	- 42.8	- 2.8
400	- 14.9	- 40.8	1.4
500	- 14.4	- 39.7	5.5
600	- 14.1	- 39.1	9.4
800	- 13.6	- 38.4	17.1

TABLE II. Atomic positions of surface atoms in modified (100)-(2×1):H monohydride.

Displacements of carbon atoms are given with respect their ideal bulk-terminated positions, while hydrogen atom positions are listed with respect to the carbon atom to which they are bonded. Atom labels refer to Fig. 2; an asterisk refers to a radical center. The structures shown in Figs. 1b, 2b and 2d are symmetric about the dimer center.

Displacements (Å) along [011]		[0 $\bar{1}$ 1]	[100]
(2×1):H (Fig. 1b)			
C1	0.447	0.000	- 0.057
C3	0.066	0.000	0.027
H1	- 0.437	0.000	1.021
(2×1):H - H (Fig. 2a)			
C1*	0.406	0.000	- 0.020
C2	- 0.380	0.000	- 0.048
H	- 0.478	0.000	1.014
(2×1):H - 2H (Fig. 2b)			
C1	0.519	0.000	- 0.106
(2×1):H + H (Fig. 2c)			
C1*	0.033	0.000	- 0.069
C2	0.044	0.000	0.007
H1	- 0.380	0.000	1.034
H1'	- 0.933	0.000	0.566
H2'	0.746	0.000	0.807
(2×1):H + 2H (Fig. 2d)			
C1	- 0.023	0.000	- 0.014
H1	- 1.005	0.000	0.399
H2	0.540	0.000	0.949



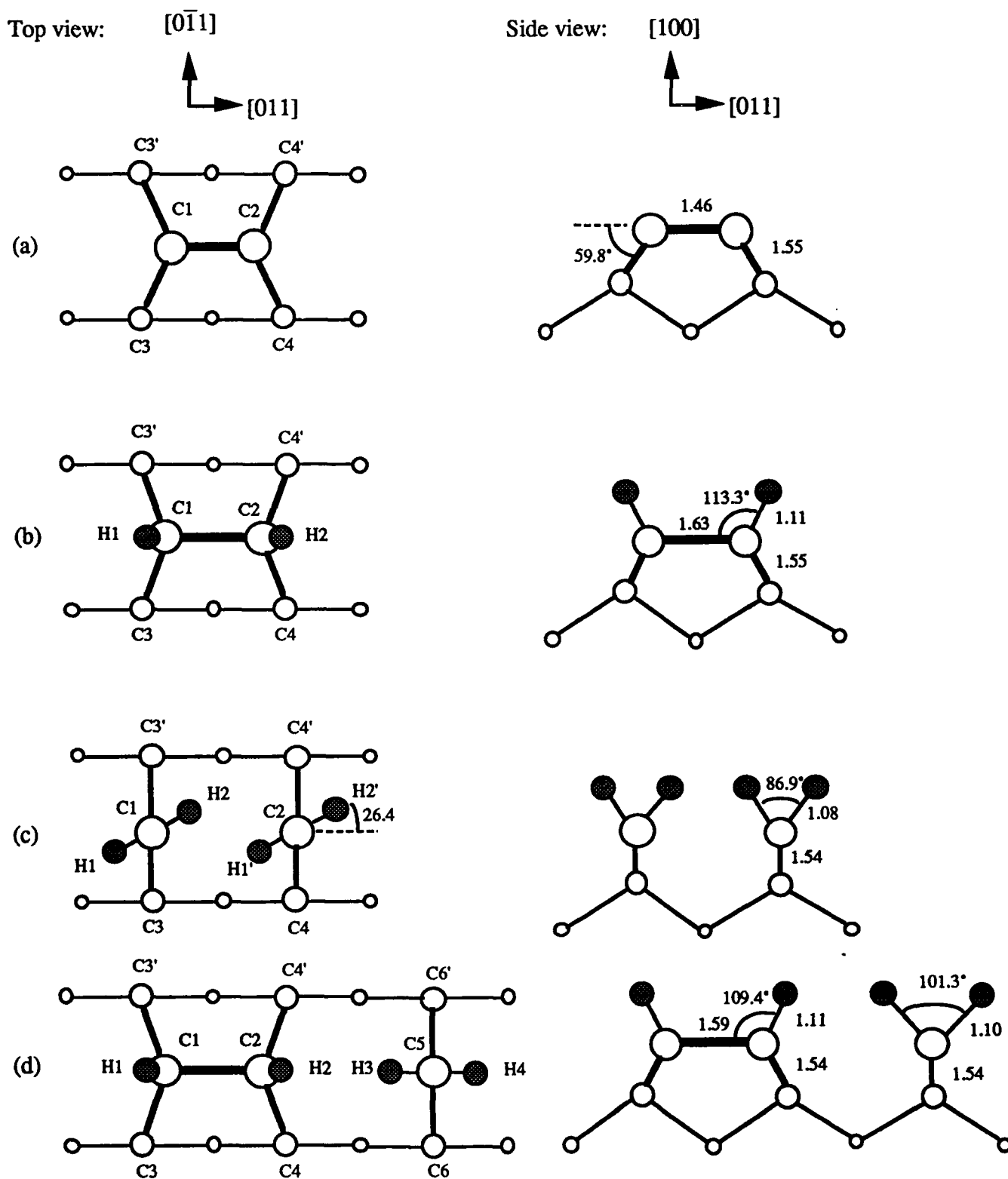


FIG. 1. Top and side views of atomic structures of clean and hydrogenated diamond (100) surfaces: (a) (2×1); (b) (2×1):H; (c) (1×1):2H; and (d) (3×1):1.33H. Bond lengths: Å. ○, ○, and ○: carbon atoms in top, second, and third layers, respectively. ●: hydrogen atoms.

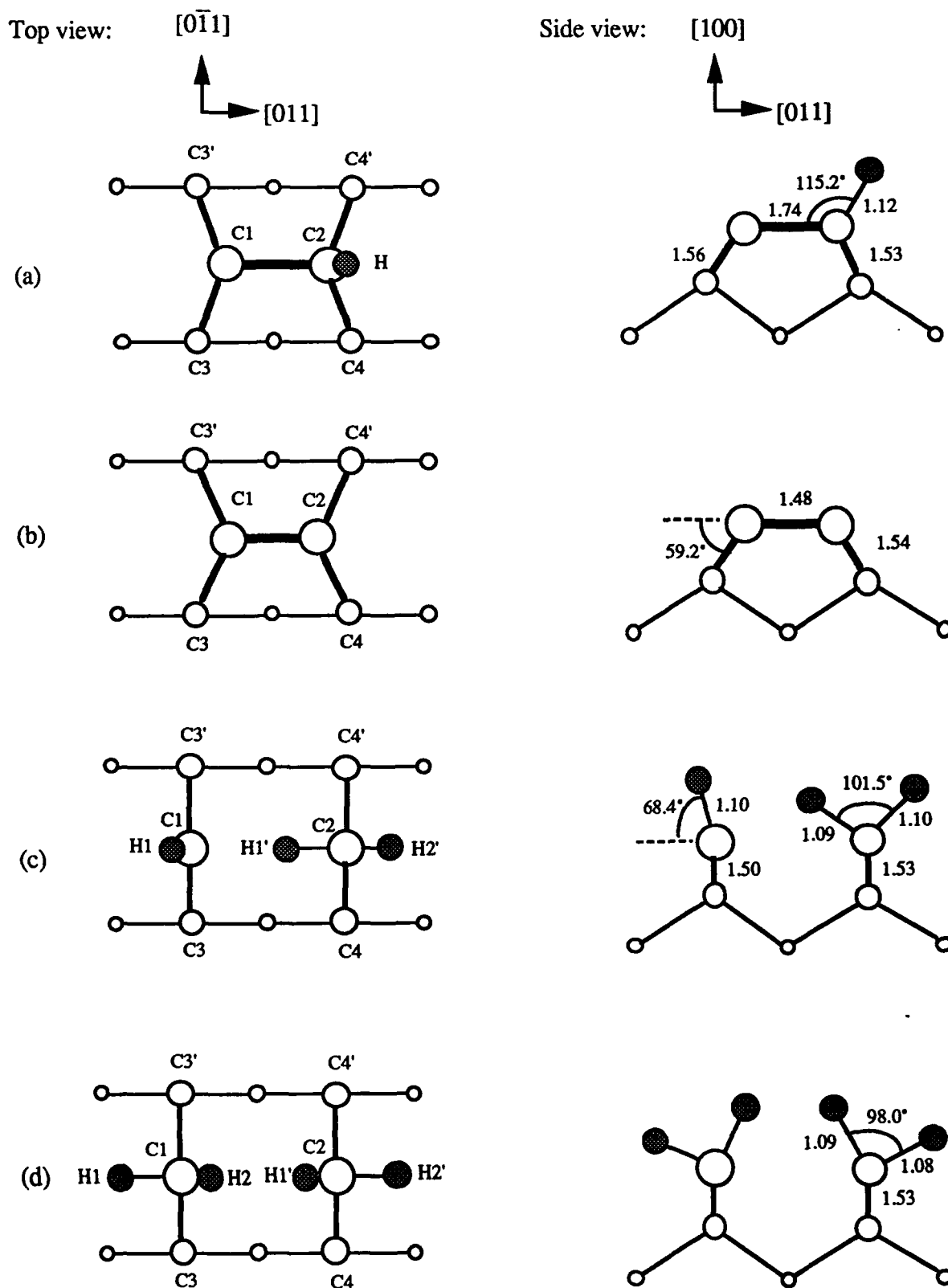


FIG. 2. Top and side views of structures of diamond (100)-(2×1):H surface after: (a) abstraction of H; (b) abstraction of two H atoms; (c) insertion of H; and (d) insertion of two H atoms.